Hartree-Fock Approximation and Entanglement

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Abstract

The relation between the correlation energy and the entanglement is analytically constructed for the Moshinsky's model of two coupled harmonic oscillators. It turns out that the two quantities are far to be proportional, even at very small couplings. A comparison is made also with the 2-point Ising model.

1   Introduction

The concept of entanglement has been recently considered by many authors [1] in connection with several properties of the quantum systems and as a potential resource in quantum computation and information processing. Moreover, entanglement has also been recognized to play an important role in the study of many particle quantum systems [2] and experimental measurement have demonstrated that it can affect macroscopic properties of the condensed matter [3]. However, a new area of research has been opened by [4], where it was argued that the entanglement (a quantum observable) can be used in evaluating the so-called correlation energy: that is the difference between the true eigenvalue energy of a given molecular system, composed by identical components, with respect to that one prescribed by the Hartree - Fock (HF) approximation method. In [5] the case of the formation of the Hydrogen molecule was discussed, and a qualitative agreement between the von Neumann entropy of either atom (measuring the entanglement of formation of the whole system) and the correlation energy as functions of the inter-nuclear distance was shown. However, the extension of this idea to multi-atomic molecules and its effectiveness remains still unclear [6,7]. The correlation energy in this context is an artifact of the approximation

1

procedure, then it is not a physical observable and, by second, it can be modified by the adopted method of calculations. In this sense the conjecture of [5] is not a well posed question and the answer to it must be only qualitative. Nevertheless, folk says that still entanglement has to play some role in taking into account the difference between the approximated computation of the (fundamental) energy level for a typical factorized wave function, as provided by the Hartree-Fock approximation, and the "true" energy eigenvalue.

This paper is devoted to a deeper analysis of it, trying to find an operative and quantitative estimation of the entanglement effects on the energy level evaluation by approximated methods. Better, one would like to clarify if the correlation energy is in a one-to-one correspondence with the entanglement of the fundamental state of bipartite systems. To this aim we analyze a very simple model of coupled harmonic oscillators introduced by M. Moshinsky about 40 years ago in the paper [8], and try to arrive to a quantitative measurement of the entanglement effects on the correlation energy.

In Sec. 2 we briefly review the Moshinsky's model, pointing out the goodness of the HF approximation for the fundamental state, both considering the correlation energy and the fidelity with respect to the exact solution and for weak couplings of the two oscillators. In Sec. 3 we evaluate the von Neumann entropy, which is the unique measure of entanglement for pure states, for the fundamental state of the Moshinsky's model, by tracing out the density matrix operator w.r.t. one of the component oscillator. Eigenvalues of the reduced density matrix are computed by discussing certain integral equations. In order to compare the von Neumann entropy and the correlation energy, in Sec. 4 we consider the minimized mean squared deviations of the two quantities. A discussion of the relative deviations is also performed. Furthermore an analytic expression of the entropy in terms of the correlation energy is provided. A comparison with the analogous expressions for the two point Ising model is discussed. Asymptotic formulae for very small couplings (or correlation energy) are considered at the end. Some final remarks are addressed in the Conclusions.

2   The Moshinsky's Model

In order to evaluate the efficiency and how good the HF mean field method is in computing quantum states, Moshinsky in [8] proposed a very simple, but non trivial, model of two coupled spin-$\frac{1}{2}$ harmonic oscillators in 3 dimensions, in which all computations can be analytically performed up to

the end.

In adimensional unities, the Hamiltonian of the model reads

$$\hat{H} = \frac{1}{2}\left(\vec{p}_1^{\,2} + \vec{p}_2^{\,2} + \vec{r}_1^{\,2} + \vec{r}_2^{\,2}\right) + \frac{1}{2}K\left(\vec{r}_1 - \vec{r}_2\right)^2, \qquad (1)$$

where $\vec{r}_i$ and $\vec{p}_i$ denote the position and the momentum operators of the i-th particle, respectively. The constant K parametrizes the interaction strength of a supplementary harmonic coupling between the two oscillators. One can interprete such as a model for two identical interacting atoms (or molecules). Thus, the coupling would represent the interatomic interaction, which one can conjecture weaker than the electron-nucleus interaction. Thus, we will dwell upon the case $0 \leq K \leq 1$ and the coupling term in (1) will be considered as a perturbative term. So changing the value of K may be interpreted as a change into the interatomic interaction. Finally, let us observe that since we are interested into the fundamental state, the spinorial aspect of the problem is not relevant. In fact, the total spin state must be singlet. For self-consistency of the present paper, here review the Moshinsky's results.

The energy spectrum of the system can be easily computed in the form

$$E_{n,m} = \frac{3}{2}\left(1 + (1 + 2K)^{1/2}\right) + n + m(1 + 2K)^{1/2}, \qquad (2)$$

where m and n are positive integers or 0. For any K the spectrum shows degeneracy, partially broken for $K > 0$. However, the lowest level is always simple. Moreover, eigenvalue crossings occur for higher eigenvalues at isolated points of K.

The normalized wave function of the fundamental level is given by

$$\left|\Psi_0\left(\vec{R},\vec{r}\right)\right\rangle = \pi^{-3/2}(1+2K)^{3/8}e^{-R^2/2}e^{-(1+2K)^{1/2}r^2/2}\left|\frac{1}{2},\frac{1}{2},0,0\right\rangle, \quad (3)$$

where the mean and relative position have been defined, $\vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{\sqrt{2}}$ and $\vec{r} = \frac{\vec{r}_1 - \vec{r}_2}{\sqrt{2}}$ respectively. Looking at the spin state of the system one can see that it is always entangled. So the question is if also the positional factor has the properties of an entangled state.

Applying the standard HF mean field approximation to the ground state, one is led to the wave function
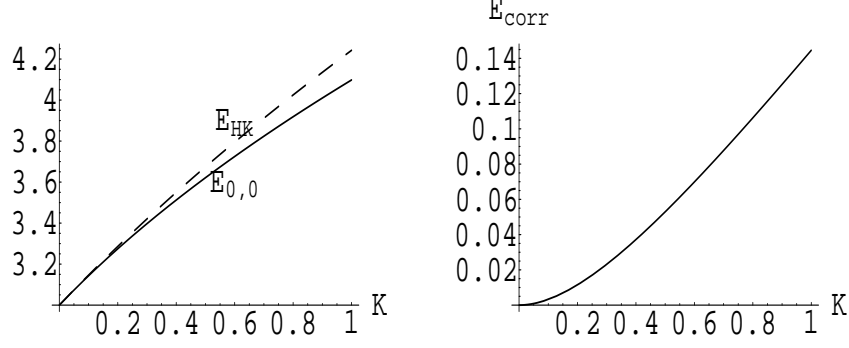
Figure 1: Exact and HF approximated fundamental level (on the left). Correlation Energy (on the right)

$$\left| \Psi_{\mathrm{HF}} \left(\vec{R}, \vec{r} \right) \right\rangle = \pi^{-3/2} (1+K)^{3/4} e^{-(1+K)^{1/2} (R^2 + r^2)/2} \left| \frac{1}{2}, \frac{1}{2}, 0, 0 \right\rangle, \quad (4)$$

corresponding to the approximated eigenvalue

$$E_{\mathrm{HF}} = 3(1+K)^{1/2}. \tag{5}$$

Defining the *correlation energy* as

$$E_{\mathrm{corr}} = E_{\mathrm{HF}} - E_{0,0} = 3\sqrt{1+K} - \frac{3}{2} \left(1 + \sqrt{1+2K} \right), \tag{6}$$

one obtains a first indication of how good the HF approximation is. For simplicity this is reported in Fig. 1. Of course, by Ritz's theorem one has $E_{\mathrm{HF}} \geq E_{0,0}$, but the approximation looks very good for small K, indeed they differ at the second order near $K = 0$ as

$$E_{\mathrm{corr}} = \frac{3K^2}{8} - \frac{9K^3}{16} + O\left(K^4 \right), \tag{7}$$

so that the relative error is less than 3.5% in the range of $0 \leq K \leq 1$. Moreover, the explicit expression of the overlap (or the squared fidelity) of the exact and the HF wave function $|\langle \Psi_{\mathrm{HF}} | \Psi_0 \rangle|^2$ as a function of K is

$$|\langle \Psi_{\mathrm{HF}} | \Psi_0 \rangle|^2 = \frac{64(1+K)^{3/2}(1+2K)^{3/4}}{\left(K + \left(1 + \sqrt{1+K} \right) \left(1 + \sqrt{1+2K} \right) \right)^3}, \tag{8}$$
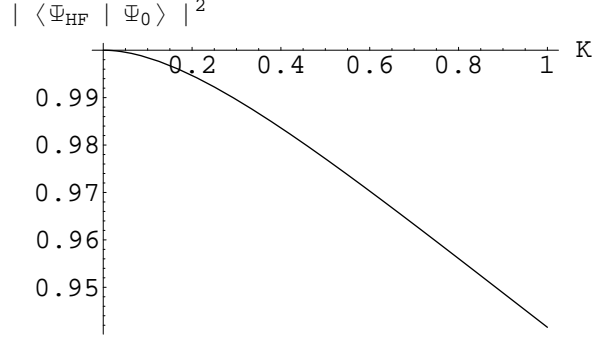
4

Figure 2: Overlap of the HF and exact ground state.

the graph of which is shown in Fig. 2. It is immediate to see that the distance between the two wave-functions is less than 95% for $0 \leq K \leq 1$. Thus, one can figure out that adding to the HF state further corrections surely improve the estimations of the energy eigenvalue and increase the fidelity, but the simplest factorized expression in (4) will be lost. Indeed, this is the case if one considers the exact expression of $\Psi_0(\vec{R},\vec{r})$ in (3). Qualitatively this means that the two oscillators in the correct fundamental state are entangled, contrary to what happens in the approximated state. Thus, one would like to attribute the mismatch between the energy of the two states (i.e. E_{corr}) to the entanglement properties. We will analyze this idea in the next Section.

3   Entanglement Estimation

As it is well known, the main estimator of the entanglement for pure states is the von Neumann entropy of the reduced density matrix $\hat{\rho}_1$ of one of the component subsystems, i.e.

$$S_{\mathrm{vN}}\left[\hat{\rho}_1\right] = -\mathrm{Tr}\left[\hat{\rho}_1\,\log_2\hat{\rho}_1\right],\ \mathrm{with}\ \hat{\rho}_1 = \mathrm{Tr}_2\left[\hat{\rho}\right] \qquad (9)$$

where in the second relation one has traced out only with respect to the second subsystem, when a proper basis of states has been chosen in the Hilbert space of the whole system. In the position - spin representation the complete system density matrix ρ for the fundamental state (3) is given by

5

$$\hat{\rho}_0 = |\Psi_0\rangle\langle\Psi_0| = \left|\frac{1}{2},\frac{1}{2},0,0\right\rangle\left\langle\frac{1}{2},\frac{1}{2},0,0\left|\rho\left(\vec{r}_1,\vec{r}_2,\vec{r}'_1,\vec{r}'_2\right)\right.\right., \qquad (10)$$

$$\rho\left(\vec{r}_1,\vec{r}_2,\vec{r}'_1,\vec{r}'_2\right) = \pi^{-3}(1+2K)^{3/4}e^{-\left(R^2+R'^2\right)/2}e^{-(1+2K)^{1/2}\left(r^2+r'^2\right)/2},$$

$$(11)$$

where one has introduced the supplementary variables $\vec{R}' = \frac{\vec{r}'_1+\vec{r}'_2}{\sqrt{2}}$ and $\vec{r}'$ $= \frac{\vec{r}'_1-\vec{r}'_2}{\sqrt{2}}$.

An analogous expression holds for the $|\Psi_{\mathrm{HF}}\rangle$ state (4). The main difference between the two functions is that in the latter case the density matrix reduces in just the product of gaussian normal distributions in the real variables $(\vec{r}_1,\vec{r}_2,\vec{r}'_1,\vec{r}'_2)$, with the same variance. Instead, in the case of density matrix (10) the different coefficients in front of $(R^2+R'^2)$ and $(r^2+r'^2)$ make the presence of mixed (entangling) terms of the form $\vec{r}_1\cdot\vec{r}_2$ and $\vec{r}'_1\cdot\vec{r}'_2$. This has consequences also at level of one particle space distribution density, which is given by

$$\rho_{0I}\left(\vec{r}\right) = \int \rho\left(\vec{r},\vec{r}_2,\vec{r},\vec{r}_2\right)d\vec{r}_2 = \frac{2^{3/2}\,(2K+1)^{3/4}}{\pi^{3/2}\left(\sqrt{2K+1}+1\right)^{3/2}}e^{-\frac{2\sqrt{2K+1}r^2}{\sqrt{2K+1}+1}},$$

$$(12)$$

which differs significantly from the one particle density obtained from the HF state, i.e.

$$\rho_{\mathrm{HF}I} = \frac{(K+1)^{3/4}}{\pi^{3/2}}e^{-\sqrt{K+1}r^2}, \qquad (13)$$

as, for instance, it can be graphically seen in Fig. 3 for a particular value of K. Thus, in the exact state the mean squared deviation in the position measurements of one particle, regardless the other one, results greater than in the approximated case by a factor $\left(\frac{\sqrt{1+K}\left(1+\sqrt{1+2K}\right)}{2\sqrt{1+2K}}\right)^{1/2}$. Correspondingly, the mean squared deviations for the modulus of the linear momentum are smaller, by the inverse of the above factor, in the exact case with respect to the HF one.
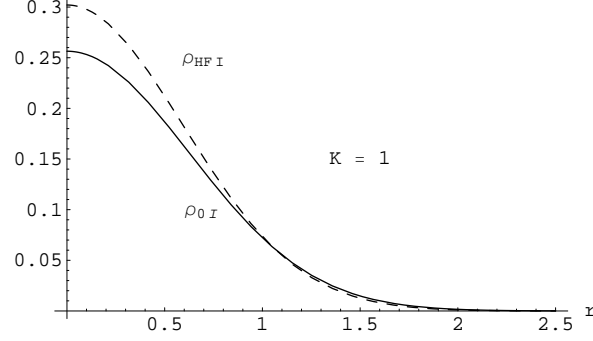
Figure 3: Exact and approximated one particle probability densities, for $K = 1$.

The analytic 1-particle spacial density matrix operator can be given in position representation $\hat{\rho}_1 = \int \rho_1 \left(\vec{r}, \vec{r'} \right) \cdot d\vec{r'}$ by the kernel

$$\rho_1 \left(\vec{r}, \vec{r'} \right) = \frac{\left(2^{3/2}(2K+1)^{3/4} \right)}{\left(\sqrt{2K+1}+1 \right)^{3/2} \pi^{3/2}}$$

$$\exp \left[\frac{\left(\sqrt{2K+1}-1 \right)^2 \vec{r} \cdot \vec{r'} - \left(K + 3\sqrt{2K+1}+1 \right) \left(\vec{r}^2 + \vec{r'}^2 \right)}{4\left(\sqrt{2K+1}+1 \right)} \right], \tag{14}$$

which we have to use into expression (9) in order to compute the corresponding von Neumann Entropy. Actually, one has to take account also of the spin state. But, a well known property of the von Neumann Entropy says that

$$S_{\text{vN}} \left[\hat{\rho} \otimes \hat{\sigma} \right] = S_{\text{vN}} \left[\hat{\rho} \right] + S_{\text{vN}} \left[\hat{\sigma} \right], \tag{15}$$

for any factorized density operator $\hat{\rho} \otimes \hat{\sigma}$. Since this is the case for the system we are considering, where the reduced matrix in the spin space state is $\frac{1}{2}$ **1** proportional to the identity matrix, the von Neumann Entropy for the one-particle subsystem can be defined modulo a constant term equal to 1.

Furthermore, the expression (9) becomes $S_{\text{vN}}[\hat{\rho}_1] = -\sum_i \mu_i \, log_2 \left(\mu_i \right)$ in terms of the eigenvalues μ_i of the operator $\hat{\rho}_1$, which is acting on the infinite dimensional space of squared sommable functions. So, the eigenvalue problem for $\hat{\rho}_1$ can be written in the form

7

$$\int \rho_1 \left(\vec{r}, \vec{r'} \right) u \left(\vec{r'} \right) d\vec{r'} = \mu \, u \left(\vec{r} \right). \tag{16}$$

As one can see from Eq. (14), the kernel of this integral equation is symmetric. Moreover, it is of Hilbert-Schmidt type, since the coefficient of $\vec{r'}^2$ is negative. So the spectrum is real and discrete. Finally, in cartesian coordinates it can be decomposed in the product of three one-dimensional kernels with the same gaussian structure

$$\tilde{\rho}_{(}x, x') = \frac{2^{1/2}(2K+1)^{1/4}}{\left(\sqrt{2K+1}+1\right)^{1/2}\pi^{1/2}}$$
$$\exp\left[\frac{\left(\sqrt{2K+1}-1\right)^2 x \, x' - \left(K+3\sqrt{2K+1}+1\right)\left(x^2+x'^2\right)}{4\left(\sqrt{2K+1}+1\right)} \right]. \tag{17}$$

Accordingly, the eigenfunctions of Eq. (16) can be factorized in the product of three functions, each of them depending only on one real variable. Thus we put for the eigenfunctions and the eigenvalues

$$u_{l,m,n} \left(\vec{r} \right) = w(x)w_m(y)w_n(z), \ \mu_{l,m,n} = \nu_l \nu_m \nu_n, \tag{18}$$

so that the problem is reduced to solve the integral spectral problem in one dimension

$$\int \tilde{\rho}_{(}x, x')w_l(x')dx' = \nu_l \, w_l(x). \tag{19}$$

Recalling the standard formulae for gaussian integrals [9]

$$\int_{-\infty}^{\infty} x'^i e^{2qx'-px'^2} \, dx' = \frac{1}{2^{i-1}p}\sqrt{\frac{\pi}{p}} \, \partial_q^{i-1}\left(qe^{\frac{q^2}{p}} \right), \tag{20}$$

it is natural to look for solutions of Eq. (19) of the form

$$w_l(x) = P_l(x)e^{-\delta x}, \tag{21}$$

where $P_l(\mathrm{x})$ is a polynomial of degree l in the variable x and δ is a real positive coefficient.

Substitution of the expression (21) in Eq. (19) leads to a pure polynomial expression iff one sets
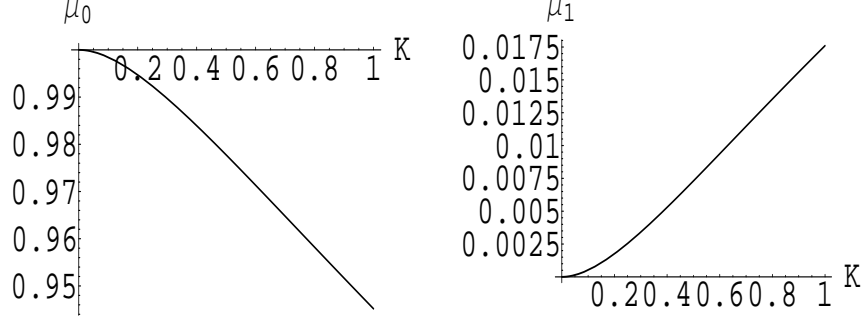
$$\delta = \frac{1}{2}(1+2K)^{1/4}. \tag{22}$$

Figure 4: The eigenvalues μ_0 and μ_1 of the reduced density operator $\hat{\rho}_1$.

Then, Eq. (19) reduces to $(l+1)$-dimensional linear eigenvalue problem for the coefficients of x in the polynomial $P_l(x)$. However, the particular form of the coefficients in the r.h.s. of formula (20) makes this problem triangular, so one can easily provide the non degenerate spectrum

$$\nu_l = C\,c^{\,l}, \tag{23}$$

where

$$
\begin{aligned}
C &= \frac{2\sqrt{2}(1+2K)^{1/4}}{\sqrt{1+K+2(1+2K)^{1/4}+3\sqrt{1+2K}+2(1+2K)^{3/4}}}, \\
c &= \frac{1+K-\sqrt{1+2K}}{1+K+2(1+2K)^{1/4}+3\sqrt{1+2K}+2(1+2K)^{3/4}}.
\end{aligned}
$$

Of course, these eigenvalues are positive and their sum is equal to 1, because related to a matrix density operator. On the other hand, accordingly to (18) the eigenvalues of the one-particle density matrix (14) are given by

$$\mu_k = C^3 c^{\,l+m+n} = C^3 c^k, \; k \, \epsilon \, \mathbb{N} \cup \{0\}, \tag{24}$$

thus the eigenvalue μ_k is degenerate of order

$$\deg[\mu_k] = \frac{k^2}{2} + \frac{3k}{2} + 1. \tag{25}$$

For comparison in Fig. 4 we report the graphs of μ_0 and μ_1. Hence, if we are allowed to interpret the eigenvalues of the density matrix operator
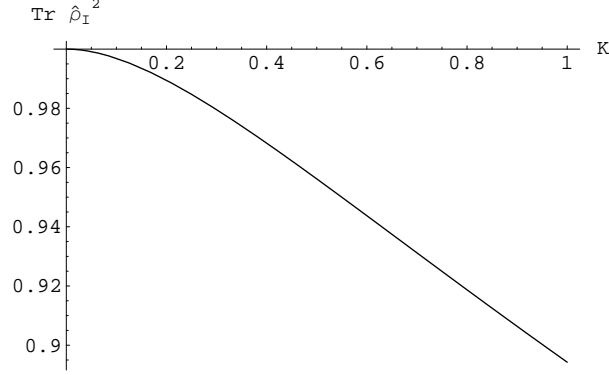
9

Figure 5: The trace of $\hat{\rho}_1^2$, as a function of the coupling constat K. The state of one the Moshinsky's oscillators becomes more mixed for increasing K.

$\hat{\rho}_1$ as the probabilities to find the one particle subsystem in the states of a K-parametrized family of harmonic oscillators, for the fundamental one it is very close to 1 and slowly decreasing in K. At $K \approx 1$, the probability to find it in the first excited state is about 1.76% and exponentially smaller for the highest excited states. The lack of coherence can be estimated also by computing the Trace $[\hat{\rho}_1^2]$. Indeed this quantity is 1 only if it corresponds to a pure state, but in the present case one has

$$\text{Tr}\left[\hat{\rho}_1^2\right] = \frac{8(1+2K)^{3/4}}{\left(1 + \sqrt{1+2K}\right)^3}, \tag{26}$$

which is a decreasing function in K, as can be seen from Fig. 5.

Now, we are in the condition to compute the von Neumann entropy, by rewriting formula (9) as

$$S_{\text{vN}}\left[\hat{\rho}_1\right] = -\sum_{k=0}^{\infty} \deg\left[\mu_k\right] \mu_k \log_2 \mu_k = \tag{27}$$

$$\frac{3}{\ln[4]}\left\{2\left(1+\chi^2\right)\ln\left[1+\chi\right] - 2\chi\,ln\left[4\chi\right] - (-1+\chi)^2\ln\left[-1+\chi^2\right]\right\}\chi^{-1},$$

where

$$\chi = (1+2K)^{\frac{1}{4}}. \tag{28}$$

A graphic of $S_{\text{vN}}[\hat{\rho}_1]$ is given in Fig. 6 for the range of $0 \leq K \leq 1$.
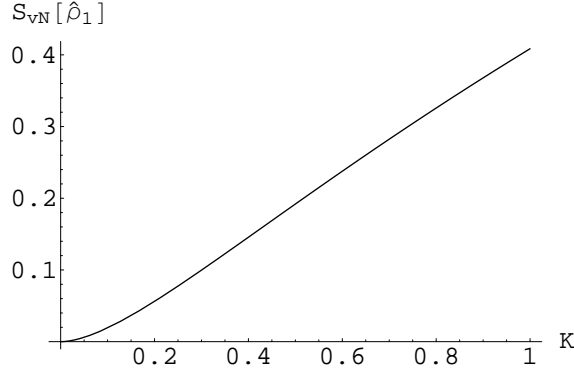
Figure 6: The entanglement of the Moshinsky's model as a function of the coupling constat K

Although in the present case the entropy is not upper bounded, since we are dealing with a system with an infinite-dimensional Hilbert space, the expression (27) is very to the analogous one for the 2-point Ising model [5,10], for which the 1-particle von Neumann entropy and the correlation energy are

$$S_{\text{vN}}^{2-\text{Ising}}[\hat{\rho}_1] = -\frac{1}{\sqrt{4+\lambda^2}\,ln[4]} \tag{29}$$

$$\left\{ \left(-2 + \sqrt{4+\lambda^2} \right) ln \left[\tfrac{1}{2} - \tfrac{1}{\sqrt{4+\lambda^2}} \right] + \left(2 + \sqrt{4+\lambda^2} \right) ln \left[\tfrac{1}{2} + \tfrac{1}{\sqrt{4+\lambda^2}} \right] \right\},$$

$$E_{\text{corr}} = \sqrt{4+\lambda^2} - 2 \ , \tag{30}$$

where λ is the normalized ferromagnetic coupling.

For large K the entropy $S_{\text{vN}}[\hat{\rho}_1]$ increases logarithmically according to the expansion at infinity

$$S_{\text{vN}}[\hat{\rho}_1] \approx \frac{3\,ln[K]}{4\,ln[2]} - \frac{21}{4} + \frac{3}{ln(2)} + O\left[\frac{1}{K^{1/2}} \right].$$

On the other hand, the behavior of $S_{\text{vN}}[\hat{\rho}_1]$ near K = 0 can be described by its series expansion

$$S_{\text{vN}}[\hat{\rho}_1] = \left(\frac{3}{4} + \frac{3}{16\,ln(2)} \right) K^2 - \frac{3K^3}{2} + \left(\frac{177}{64} - \frac{189}{512\,ln(2)} \right) K^4$$

$$- \frac{3K^2 \left(16 - 32K + 59K^2 \right)}{128\,ln(2)}\, ln(K) + O\left(K^5 \right), \tag{31}$$

11

but this approximation becomes inaccurate very rapidly. From the above expression one sees the asymptotic behavior of the entropy close to 0 is controlled by a logarithmic term, differently from the correlation energy (6), which has a pure power expansion. Then, we cannot expect a great similarity between the two functions, also at very small values of K.

4 Comparing Entropy and Correlation Energy

The comparison of entropy and correlation energy requires at least a common scale of unities, the former being a pure number. So, the simplest proposal is to study a family of deviation functions of the form

$$\Delta(\alpha, K) = \alpha S_{\text{vN}} [\hat{\rho}_1] - E_{\text{corr}}, \tag{32}$$

where α is a parameter to be properly chosen. The choice of α can be done in several ways but, trying to minimize the values of $\Delta(\alpha)$ in a range of K, a criterion could be given by the minimization of the squared deviations functional

$$I[\alpha] = \int_0^1 \Delta(\alpha, K)^2 \, dK. \tag{33}$$

Quite arbitrarily, the domain of integration is determined by our interest to small perturbations of the 2-independent harmonic oscillators system. This is equivalent to set

$$\alpha_{\min} = \frac{\int_0^1 S_{\text{vN}} [\hat{\rho}_1] E_{\text{corr}} dK}{\int_0^1 S_{\text{vN}} [\hat{\rho}_1]^2 \, dK} \approx 0.318949, \tag{34}$$

where a numerical evaluations is needed because of the intricate form of the integrand functions. The graphic of the function $\Delta(\alpha_{\min}, K)$ is given in Fig. 7 . An estimation of the relative deviations of the correlation energy with respect to the entropy is given in Fig. 7. In both cases we have considered the relative deviation at the minimum of the squared deviation functional (31). As one can see, in both cases the relative error is quite big, particularly close to 0, where the behavior of these functions are largely controlled by logarithmic or cuspidal singularities. In particular, while in the expansion of $\Delta(\alpha_{\min}, K)/ S_{\text{vN}} [\hat{\rho}_1]$ a finite cuspidal singularity appears at 0, i.e.

$$\frac{|\Delta(\alpha_{\min}, K)|}{S_{\text{vN}} [\hat{\rho}_1]} = 0.035439 + O(K), \quad \frac{d}{dK} \left(\frac{|\Delta(\alpha_{\min}, K)|}{S_{\text{vN}} [\hat{\rho}_1]} \right) \simeq \frac{-8.20851 \times 10^{-16}}{K^4},$$
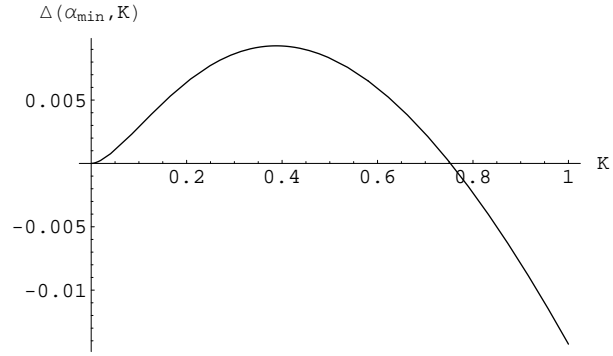
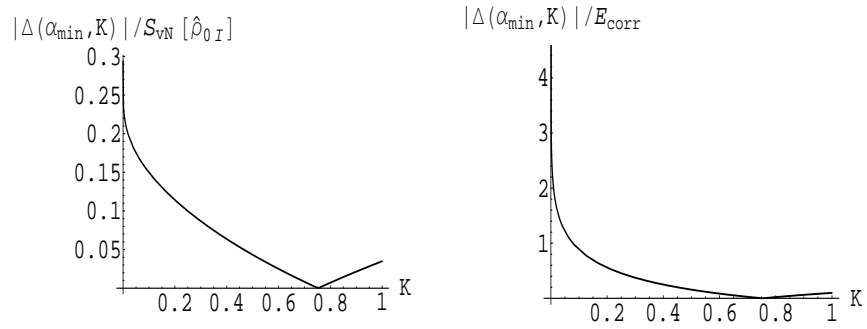Figure 7: A plot of the minimized deviations between entropy and correlation energy.

Figure 8: The relative minimized deviations between entropy and correlation energy.

13

while the relative deviation with respect to the correlation energy shows a true logarithmic divergence as

$$\frac{|\Delta\left(\alpha_{\min}, K\right)|}{E_{\text{corr}}} = 1 + 1.14945 \times 10^{-16} \ln\left(K\right) + O(K), \qquad (35)$$

making very questionable the meaning of these quantity, taking into account also the tiny absolute values of the expansion coefficients.

On the other hand, correlation energy and entropy look almost proportional in the restricted range $\sim 0.6 \leq K \leq 0.8$. In this region of the K parameter it is confirmed in explicit way how the correlation energy is a direct effect of the entanglement. In general such a relation is less obvious. In fact, first let us observe that both functions $S_{\text{vN}}\left[\hat{\rho}_1\right]$ and E_{corr} are both monotonically increasing in K. Therefore, since E_{corr} is a quite simple algebraic function on the coupling constant, it can be easily inverted and replaced into $S_{\text{vN}}\left[\hat{\rho}_1\right]$, obtaining again a one-to-one correspondence, say $\tilde{S}_{\text{vN}}\left(E_{\text{corr}}\right)$, the expression of which is a little involved, actually

$$\tilde{S}_{\text{vN}}\left(E_{\text{corr}}\right) = \frac{1}{\sqrt{2\tau+3}\,ln(4)}\left\{4\sqrt{3}(\tau+3)\,ln\left(\sqrt{6\tau+9}+3\right)\right. \qquad (36)$$
$$-2\sqrt{3}\,ln(6)\left(\tau+3\right) - 2\left(\sqrt{3}(\tau+3)-3\sqrt{2\,\tau+3}\right)\,ln(\tau)$$
$$\left.-3\sqrt{2\,\tau+3}\,ln(2\,\tau+3)-3\sqrt{2\tau+3}\,ln(12)\right\},$$

where we have introduced the auxiliary variable $\tau = E_{corr} + \sqrt{2}\sqrt{E_{corr}\left(E_{corr}+3\right)}$. A plot of this function is given in Fig. 9. The analogous expression for the 2-point Ising model results directly by substituting E_{corr} given in Eq. (30) into the expression (29) for the entanglement. A plot of this function is as is also sketched in Fig. 9.

In both cases the entanglement is an increasing function of the correlation energy. In particular, one can search explicit but approximated expressions of the entanglement for small values of E_{corr}, corresponding to small couplings. Indeed, including logarithmic corrections at the lowest order near $E_{\text{corr}} \approx 0$, one obtains

$$\tilde{S}_{\text{vN}}\left(E_{\text{corr}}\right) \approx \frac{\left(1+\,ln[6]-ln\left[E_{\text{corr}}\right]\right)}{2\,ln[2]} E_{\text{corr}}, \qquad (37)$$

$$\tilde{S}_{\text{vN}}^{2-\text{Ising}}\left(E_{\text{corr}}\right) \approx \frac{\left(1+2\,ln[2]-ln\left[E_{\text{corr}}\right]\right)}{4\,ln[2]} E_{\text{corr}}, \qquad (38)$$

for the Moshinsky's oscillators and the 2-point Ising model, respectively. As one can see, the two asymptotic formulae above are very similar, but not
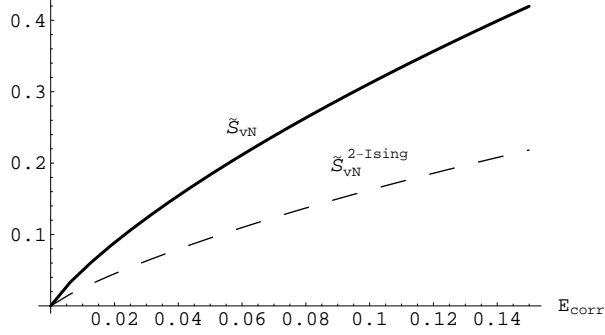
14

Figure 9: The entanglement as a function of the correlation energy for the Moshinsky's model (continuous curve) and for the 2-point Ising model (dashed curve).

sufficient to argue that there exists a general argument allowing to compute the coefficients appearing in the above developments.

For large perturbations, or equivalently for $E_{\text{corr}} \to \infty$, one has the asymptotic expansions

$$\tilde{S}_{\text{vN}}\left(E_{\text{corr}}\right) = \frac{3\left(2 + \sinh^{-1}(1) - ln(24)\right)}{ln(4)} + \frac{3\,ln\left(E_{\text{corr}}\right)}{2\,ln(2)} + O\left(\frac{1}{E_{\text{corr}}}\right) \quad (39)$$

for the Moshinsky's model, while for the finite levels 2-point Ising model the entanglement will approach the limiting value 1 as

$$\tilde{S}_{\text{vN}}^{2-\text{Ising}} = 1 - \frac{2}{ln(2)E_{\text{corr}}^2} + O\left(\frac{1}{\text{E}_{corr}^3}\right). \quad (40)$$

Concerning the singular behavior of the entanglement as a function of the correlation energy it does not seem related to the specific way of its estimation. In fact, in alternative to the von Neumann entropy one can use the concurrence [10], which uniquely defines the entropy at least for the Ising model (see Eq. 29). In this case the concurrence takes the form

$$C^{2-Ising} = \frac{\lambda}{\sqrt{\lambda^2 + 4}}. \quad (41)$$

Furthermore, expressed in terms of the correlation energy in (30), it becomes

$$C^{2-Ising} = \frac{\sqrt{E_{\text{corr}}\left(E_{\text{corr}} + 4\right)}}{E_{\text{corr}} + 2}. \quad (42)$$

15

As one can see, the first derivative of this expression contains an algebraic singularity at 0 instead of a logarithmic one, as it shown by Eq. (42), and it has a monotonic algebraic increasing to the limiting value 1.

Inspired by [10], one can define the analogous of the concurrence for the Moshinsky's system (at least limiting ourselves to the set of considered ground states) as

$$C = 1 - Tr[\hat{\rho}_1^2], \qquad (43)$$

which takes values in the range $[0, 1[$. It is invariant under local unitary transformations on the separate oscillators (reduced to changes of phases) and provides a unique mapping for S_{vN} $[\hat{\rho}_1]$, by using Eq. (28) into (26) and, then, replacing into (27).

As a function of the correlation energy, the above defined quantity takes the form

$$C(E_{corr}) = 1 - \frac{3\sqrt{3}\left(2E_{corr} + 2\sqrt{2}\sqrt{E_{corr}\left(E_{corr} + 3\right)} + 3\right)^{3/2}}{\left(E_{corr} + \sqrt{2}\sqrt{E_{corr}\left(E_{corr} + 3\right)} + 3\right)^3}, \qquad (44)$$

which is regular in the origin, but it is not its second derivative. Again a singularity is signaling the a greater rate of increase of the entanglement with respect to the correlation energy, for small values of the latter.

One advantage of the expression (44) is that it can be easily inverted, providing a quite simple expression of the correlation energy of the Moshinsky's model in terms of the entanglement, which was one of the original motivations of the present work. Specifically, one has the correlation energy as a function of the concurrence (41)

$$E_{corr} = \frac{3}{(1-C)^{5/6}}\left[\sqrt{2C - \sqrt[3]{1-C}\left(2\sqrt{(1-C)^{4/3} - 3(1-C)^{2/3} + 2} - 3\right) - 2}\right.$$
$$\left. + (1-C)^{1/6}\left(\sqrt{(1-C)^{4/3} - 3(1-C)^{2/3} + 2} - 1\right)\right]. \qquad (45)$$

In particular, the power expansion of the above expression near 0 concurrence is given by

$$E_{corr} \approx C + \sqrt{\frac{2}{3}}\,C^{3/2} + \frac{2\,C^2}{3} + O\left(C^{5/2}\right). \qquad (46)$$

This expression gives a direct relation between the correlation energy and the entanglement via the quantity defined in (43), much simpler than by using the von Neumann entropy.
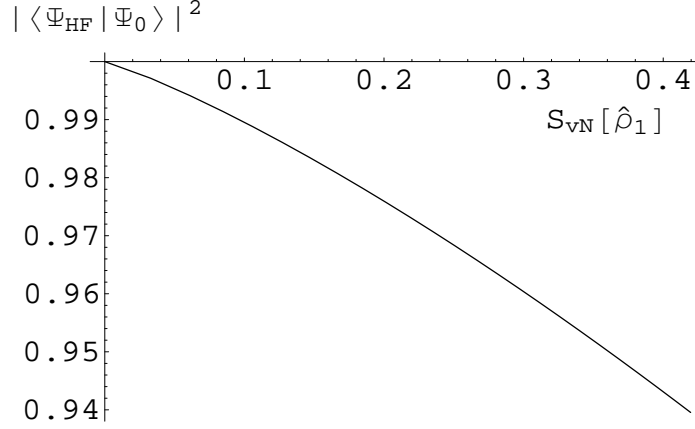
Figure 10: The overlap for HF w.r.t. the exact ground state of the Moshinsky's model entanglement as a function of the

Finally, the fidelity of the fundamental state of the Moshinsky's model with the corresponding HF state, or equivalently the overlap (8), can ex-pressed as a function of the entanglement. In some sense, we are comparing two different way to measure the "distance" between the two curves of states, even if neither quantities actually have the properties of a distance. How-ever, also in this case a monotonic function can be obtained for any pair of states corresponding to the same coupling constant K, or correlation energy E_{corr}. But, in general, an explicit expression of such a function is unknown for generic states of the Moshinsky's model. A plot of the function is shown in Fig. 10. Also for this particular situation, even if regular, the behavior at the origin possesses a singularity in its higher derivatives.

5 Conclusions

In the present paper, from point of view of the entanglement theory of quan-tum systems, we have described the relations occurring between two special curves in the space states of a family of bipartite system (the Moshinsky's model of harmonic oscillators), continuously parametrized by a coupling constant. To varying of that, one curve contains the exact ground states, the other the states provided by the HF method approximated solutions. Of course, for vanishing coupling the two curves flow out from the same state,

17

but we would characterize how they separate in terms of entanglement. The peculiarity of the latter curve is to lie always in the manifold of 0 entanglement, while the other one suffers a monotonic increasing entanglement. This could provide a measure of the "distance" between the two curves and, maybe, of the geometry of the space state around them. On the other hand, a similar, but not necessarily equivalent description is given in terms of the correlation energy, which in principle is defined only for pairs of corresponding states (at same coupling K) in the two curves. We have proved that entanglement and correlation energy are one-to-one along these curves. However some peculiarities arise. First, they are far to be proportional and only for certain intervals of the coupling constant their squared deviations can be considered small to some percentage. Second, at origin they have a quite different rate of increasing. We show that this phenomenon occurs not only in terms of the von Neumann entropy, but also by introducing an adaptation of the concurrence. From the view point of physico-chemical calculations the above observations say that an artifact of the calculation methods, the correlation energy, can be interpreted and calculated in terms of the entanglement of the wave function of the exact solution. Moreover, we have quite simple algebraic relations in terms of the concurrence (see Eq. (46)). However, at the moment we have not a general method to compute directly the coefficients of such type of expansions. These could be very useful in order to have an alternative a priori estimation of the error made in computing the correct expectation values of the energy.

We have shown also that the overlap of the exact wave functions with the corresponding HF approximations are in a one-to-one correspondence with the correlation energy and the entanglement. In particular a monotonic decreasing of the overlap occurs as a function of the entanglement, with a non analytic behavior at the origin. Differently as above, such a type of relation may be useful in the estimation of the entanglement, which could be quite complicated to compute for bipartite systems with high inner degrees of freedom, as the dimers of complex molecules (see [6-7] for instance).

Finally, we would stress that if a general principle of nature would state that it is impossible to create (or increase) entanglement between remote quantum systems by local operations [11] (in analogy with the second law of the thermodynamics), expressions like (32) may suggest proper modifications in presence of globally controlled operations, analogous to the isothermal transformations. In this respect, the true meaning of the minimizing parameter α is still obscure and could be a further direction of investigation. It could be just a case but, as noticed in [7], the properties of the function $\Delta\left(\alpha_{\min}, K\right)$ could be used to predict special configurations of the considered

physical systems, in a sort of balance between entanglement and energy.

Acknowledgements

References

[1] M. A. Nielsen and I. L. Chuang : " Quantum Computation and Quantum Information ", Cambridge University Press, Cambridge (2000).

[2] Y. Chen, P. Zanardi, Z.D. Wang, F.C. Zhang: " Entanglement and Quantum Phase Transition in Low Dimensional Spin System ", quant-ph/0407228.

[3] L. He, G. Bester and A. Zunger, cond-math/0503492 (2005).

[4] D. M. Collin, *Z. Naturforsch.* **A48**, 68 (1993).

[5] Z. Huang, S. Kais:" Entanglement as measure of the electron-electron correlation in quantum chemistry calculations", *Chem.Phys.Lett.* **413**, 1 (2005).

[6] T. Maiolo, F. Della Sala, L. Martina, G. Soliani, quant/ph/0610238, to appera in *Theor. Math. Phys.* (2007)

[7] T. Maiolo, L. Martina, G. Soliani, quant/ph/0704.0520v1. [quant-ph]

[8] M. Moshinsky:" How Good is the Hartree-Fock Approximation ?", *Am. J. Phys.* **36**, 52 (1968).

[9] I. S. Gradshteyn and I.M. Ryzhik : " Table of integrals, series, and products" ; Alan Jeffrey, editor , Academic Press, San Diego (1994).

[10] S. Hill and W. K. Wootters, *Phys. Rev. Lett.*, **78**, 5022 (1997); W. K. Wootters, *Phys. Rev. Lett.*, **80**, 2245 (1998).

[11] S. Popescu, D. Rohrlich, *Phys. Rev.* **A 56**, R3319 (1997).